Reactivity of Rhodium(I) Iminophosphine Carbonyl Complexes with Methyl Iodide

Jonathan Best,[†] John M. Wilson,[†] Harry Adams,[†] Luca Gonsalvi,*[,‡] Maurizio Peruzzini,[‡] and Anthony Haynes*[,†]

Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, U.K., and Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino (Firenze), Italy

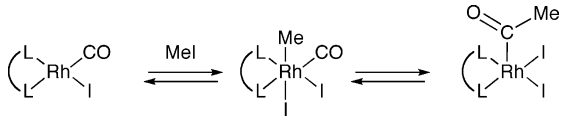
Received January 8, 2007

A series of Rh(I) iodocarbonyl complexes, [Rh(CO)I(PN^{Ar})] (**1a**−**g**), has been prepared by the reactions of $[Rh(CO)_2I]_2$ with iminophosphine ligands, $Ph_2PC_6H_4$-2-CH=NAr (PN^{Ar}; Ar = C_6H_5 (**a**), 2,6-$Me_2C_6H_3$ (**b**), 2,6-$^{i}Pr_2C_6H_3$ (**c**), 2-EtC_6H_4 (**d**), 2-$MeOC_6H_4$ (**e**), 4-$MeOC_6H_4$ (**f**), 3,5-$(CF_3)_2C_6H_3$ (**g**)). For ^{13}CO-labeled **1b**, a relatively small $^2J_{CP}$ coupling (12 Hz) showed the CO ligand to be cis to the P-donor atom of the iminophosphine. Complexes **1a**−**g** react with methyl iodide to give Rh(III) methyl or acetyl products. For complexes **1a**,**d**,**f**,**g** the reactions result in equilibria between the methyl complexes [Rh(CO)(PN^{Ar})I_2-Me] (**2**) and acetyl complexes [Rh(PN^{Ar})(COMe)I_2] (**3**), whereas the reactions of **1b**,**c**,**e** gave only the acetyl products [Rh(COMe)I_2(PN^{Ar})] (**3b**,**c**,**e**). Migratory CO insertion is promoted for systems in which the N-aryl group of the iminophosphine is bulky or contains an *o*-methoxy substituent. An X-ray structure of **3e** reveals an interaction between the Rh center and the *o*-methoxy group (Rh−O = 2.54 Å). Second-order rate constants for MeI oxidative addition to **1a**−**g** vary considerably, depending on the steric and electronic properties of the iminophosphine N-aryl substituents. The most reactive complex is **1e**, and a mechanism is proposed in which the *o*-methoxy group interacts with the Rh center to promote both oxidative addition and CO insertion.

Introduction

Bidentate chelating ligands containing phosphorus and/or nitrogen donor atoms are frequently used in organometallic chemistry and homogeneous catalysis. The steric and electronic properties of such ligands can be tuned by altering either the ligand backbone or the P- or N-bound substituents. Such modifications can be used to influence the rates of key steps in homogeneous catalytic cycles. Recently we have studied the reactivity of a range of rhodium iodo carbonyl complexes of the type [Rh(CO)(L−L)I], where L−L is a bidentate chelating ligand (e.g., dppe ($Ph_2P(CH_2)_2PPh_2$), dppms ($Ph_2PCH_2P(S)Ph_2$), or an α-diimine).[1−3] Of particular interest have been the oxidative addition reactions of these complexes with methyl iodide, which model the rate-determining step in the catalytic cycle for the rhodium/iodide-catalyzed carbonylation of methanol. Steric effects have been found to play a major role in determining the reactivity in such systems. Bulky ligand substituents tend to inhibit oxidative addition but can encourage subsequent migratory CO insertion in the Rh(III) methyl product. Thus, the bidentate ligand has a large influence on the kinetics and thermodynamics of both steps in Scheme 1, and this reaction sequence serves as a useful probe of ligand effects in general.

Scheme 1. General Mechanism for Reaction of Chelate Rh(I) Iodo Carbonyl Complexes with MeI



Here, we extend these studies to rhodium complexes of iminophosphine ligands which contain both P and N donor functions. Iminophosphine complexes have been employed for a wide variety of homogeneous catalytic processes: for example, C−C coupling reactions (Pd[4−13]), alkynylstannylation (Pd[14−16]),

* To whom correspondence should be addressed. E-mail: a.haynes@sheffield.ac.uk (A.H.).

[†] University of Sheffield.

[‡] Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici.

(1) Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A. *J. Am. Chem. Soc.* **1999**, *121*, 11233.

(2) Gonsalvi, L.; Adams, H.; Sunley, G. J.; Ditzel, E.; Haynes, A. *J. Am. Chem. Soc.* **2002**, *124*, 13597.

(3) Gonsalvi, L.; Gaunt, J. A.; Adams, H.; Castro, A.; Sunley, G. J.; Haynes, A. *Organometallics* **2003**, *22*, 1047.

(4) Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2000**, *19*, 2637.

(5) Koprowski, M.; Sebastian, R.-M.; Maraval, V.; Zablocka, M.; Cadierno, V.; Donnadieu, B.; Igau, A.; Caminade, A.-M.; Majoral, J.-P. *Organometallics* **2002**, *21*, 4680.

(6) Schultz, T.; Schmees, N.; Pfaltz, A. *Appl. Organomet. Chem.* **2004**, *18*, 595.

(7) Crociani, B.; Antonaroli, S.; Beghetto, V.; Matteoli, U.; Scrivanti, A. *Dalton Trans.* **2003**, 2194.

(8) Crociani, B.; Antonaroli, S.; Canovese, L.; Uguagliati, P.; Visentin, F. *Eur. J. Inorg. Chem.* **2004**, 732.

(9) Scrivanti, A.; Matteoli, U.; Beghetto, V.; Antonaroli, S.; Crociani, B. *Tetrahedron* **2002**, *58*, 6881.

(10) Scrivanti, A.; Beghetto, V.; Matteoli, U.; Antonaroli, S.; Marini, A.; Mandoj, F.; Paolesse, R.; Crociani, B. *Tetrahedron Lett.* **2004**, *45*, 5861.

(11) Scrivanti, A.; Beghetto, V.; Matteoli, U.; Antonaroli, S.; Marini, A.; Crociani, B. *Tetrahedron* **2005**, *61*, 9752.

(12) Scrivanti, A.; Bertoldini, M.; Matteoli, U.; Beghetto, V.; Antonaroli, S.; Marini, A.; Crociani, B. *J. Mol. Catal. A: Chem.* **2005**, *235*, 12.

(13) Crociani, B.; Antonaroli, S.; Marini, A.; Matteoli, U.; Scrivanti, A. *Dalton Trans.* **2006**, 2698.

(14) Shirakawa, E.; Nakaob, Y.; Murotab, Y.; Hiyamab, T. *J. Organomet. Chem.* **2003**, *670*, 132.

(15) Yoshida, H.; Shirakawa, E.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *Organometallics* **2000**, *19*, 5671.

10.1021/om070019b CCC: $37.00
Publication on Web 03/08/2007

alkoxycarbonylation of alkynes (Pd[17]), oligomerization and polymerization of ethylene (Ni, Pd[18−20]), CO/alkene copolymerization (Pd[21,22]), amination (Pd[23,24]), transfer hydrogenation (Ru[25,26]), and hydroboration (Rh[27]). Rhodium and iridium complexes containing iminophosphines have also been applied in studies of oxygen uptake.[28,29]

We have utilized iminophosphine ligands of the type $Ph_2PC_6H_4$-2-CH═NAr (PN^{Ar}), which are easily accessible by condensation of (diphenylphosphino)benzaldehyde with primary amines. A number of Rh(I) iodo carbonyl complexes, [Rh(CO)(PN^{Ar})I], have been synthesized with N-aryl substituents having different steric and electronic properties. Kinetic studies on the reactions of these complexes with methyl iodide reveal an unexpected steric effect on the rate of oxidative addition. It is also demonstrated that a neighboring group effect of an *o*-methoxy substituent on the iminophosphine N-aryl group can promote both oxidative addition and migratory insertion.

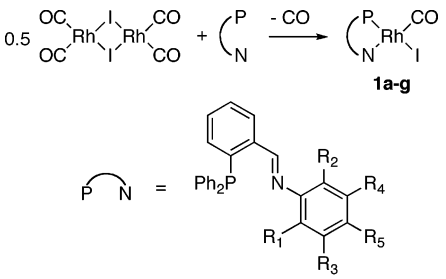
Results and Discussion

Synthesis and Characterization of Rh(I) Complexes. The iminophosphine ligands PN^{Ar} were prepared by condensation of (diphenylphosphino)benzaldehyde and the appropriate primary amine. Preparative methods have been reported previously[15,25,26] for all the ligands except those with 2-C_6H_4Et and 3,5-$C_6H_3(CF_3)_2$ substituents. Complexation to Rh(I) was achieved by reaction with the dimeric precursor $[Rh(CO)_2I]_2$ (Scheme 2).

The products [Rh(CO)(PN^{Ar})I] (**1a**−**g**) were isolated as strongly colored crystalline solids and characterized by a combination of spectroscopic and analytical methods. The ν(CO) absorptions occur between 1995 and 1998 cm^{-1} for all of the complexes except **1g** (2002 cm^{-1}), which has electron-withdrawing CF_3 substituents on the iminophosphine N-aryl group. In comparison to related Rh(I) iodo carbonyls, [Rh(CO)(dppe)I] (2011 cm^{-1}) and [Rh(CO)(ArN═C(Me)C(Me)═NAr)I] (1993−1994 cm^{-1}), these ν(CO) values lie slightly closer to those for the diimine systems.

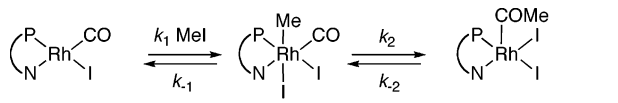
For each complex the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet between δ 40 and 48 with $^1J_{RhP}$ = ca. 170 Hz, indicating the presence of a single isomer of each complex. In the case of

Scheme 2. Synthesis of Rh(I) Complexes 1a−g



	R_1	R_2	R_3	R_4	R_5
a	H	H	H	H	H
b	Me	Me	H	H	H
c	^{i}Pr	^{i}Pr	H	H	H
d	Et	H	H	H	H
e	OMe	H	H	H	H
f	H	H	H	H	OMe
g	H	H	CF_3	CF_3	H

Scheme 3. Reactivity of Complexes 1a−g with MeI



1b ^{13}C labeling was employed in order to determine whether the CO ligand is cis or trans to the P donor of the iminophosphine ligand. Brief bubbling of ^{13}CO through a CH_2Cl_2 solution of **1b** resulted in a shift of the ν(CO) band in the IR spectrum from 1998 to 1953 cm^{-1}, consistent with exchange of the CO ligand. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of ^{13}CO-labeled **1b** each displayed a doublet of doublets ($\delta(^{31}P)$ 41.3, $^1J_{RhP}$ = 169 Hz; $\delta(^{13}C)$ 190.8, $^1J_{RhC}$ = 70 Hz, $^2J_{PC}$ = 12 Hz). The relatively small value of $^2J_{PC}$ indicates that the CO ligand is cis to phosphorus,[30,31] since a larger coupling (>100 Hz) would be expected for a carbonyl trans to phosphorus.[31] The methine proton of the imino group in **1a**−**g** displayed a signal close to δ 8.0, which appeared as either a doublet or a broadened singlet due to $^4J_{PH}$ coupling. In the ^1H NMR spectrum of **1c**, two doublets at δ 0.69 and 1.29 indicate that the methyls of the isopropyl substituents are inequivalent, due to restricted rotation about the N-aryl bond.

Reactions of Rh(I) Complexes with MeI. The reactions of complexes **1a**−**g** with MeI were monitored by FTIR spectroscopy to probe the evolution of ν(CO) absorptions of the reactants and products. The outcome was found to be dependent on the electronic and steric properties of the iminophosphine ligand. For complexes **1a**,**d**,**f**,**g**, the decay of the reactant ν(CO) band was accompanied by simultaneous growth of product absorptions at both higher frequency (2070−2073 cm^{-1}) and lower frequency (1701−1726 cm^{-1}). These bands are assigned respectively to the Rh(III) methyl species [Rh(CO)(PN^{Ar})I_2Me] (**2**), resulting from MeI oxidative addition, and Rh(III) acetyl complexes [Rh(PN^{Ar})(COMe)I_2] (**3**), formed by subsequent migratory CO insertion (Scheme 3). The methyl and acetyl species exist in equilibrium, and no single product could be isolated. On the basis of the relative intensities of the IR bands, the equilibrium constant for migratory CO insertion is larger

(16) Nakao, Y.; Hirata, Y.; Ishihara, S.; Oda, S.; Yukawa, T.; Shirakawa, E.; Hiyama, T. *J. Am. Chem. Soc.* **2004**, *126*, 15650.
(17) Scrivanti, A.; Matteoli, U.; Beghetto, V.; Antonaroli, S.; Scarpelli, R.; Crociani, B. *J. Mol. Catal. A: Chem.* **2001**, *170*, 51.
(18) van den Beuken, E. K.; Feringa, B. L.; Smeets, W. J. J.; Spek, A. L. *Chem. Commun.* **1998**, 223.
(19) Crossetti, G. L.; Dias, M. L.; Queiroz, B. T.; Silva, L. P.; Ziglio, C. M.; Bomfim, J. A. S.; Filgueiras, C. A. L. *Appl. Organomet. Chem.* **2004**, *18*, 331.
(20) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784.
(21) Reddy, K. R.; Tsai, W.-W.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *Dalton Trans.* **2002**, 1776.
(22) Pascu, S. I.; Coleman, K. S.; Cowley, A. R.; Green, M. L. H.; Ree, N. H. *J. Organomet. Chem.* **2005**, *690*, 1645.
(23) Crociani, B.; Antonaroli, S.; Bandoli, G.; Canovese, L.; Visentin, F.; Uguagliati, P. *Organometallics* **1999**, *18*, 1137.
(24) Crociani, B.; Antonaroli, S.; Canovese, L.; Visentin, F.; Uguagliati, P. *Inorg. Chim. Acta* **2001**, *315*, 172.
(25) Crochet, P.; Gimeno, J.; García-Granda, S.; Borge, J. *Organometallics* **2001**, *20*, 4369.
(26) Crochet, P.; Gimeno, J.; Borge, J.; García-Granda, S. *New J. Chem.* **2003**, *27*, 414.
(27) McIsaac, D. I.; Geier, S. J.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Inorg. Chim. Acta* **2006**, *359*, 2771.
(28) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1992**, 3371.
(29) Barbaro, P.; Bianchini, C.; Laschi, F.; Midollini, S.; Moneti, S.; Scapacci, G.; Zanello, P. *Inorg. Chem.* **1994**, *33*, 1622.
(30) Rankin, J.; Poole, A. D.; Benyei, A. C.; Cole-Hamilton, D. J. *Chem. Commun.* **1997**, 1835.
(31) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D. *Inorg. Chem.* **1988**, *27*, 4294.

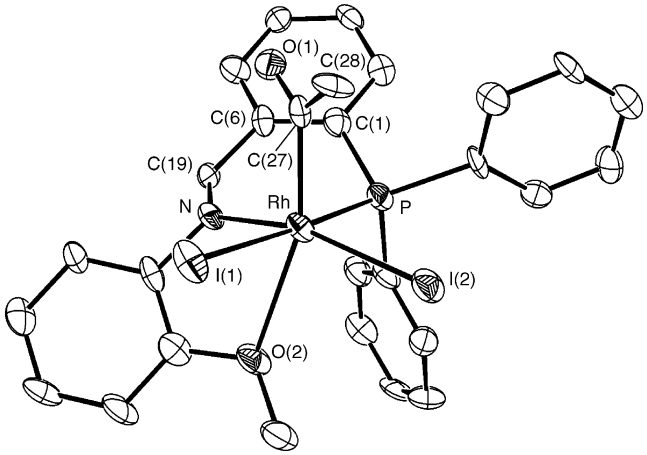


Figure 1. ORTEP diagram showing the molecular structure of **3e**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and the pentane solvent molecule are omitted for clarity.

for **2d** than for **2a**,**f**,**g**, suggesting that the extra steric bulk of an *o*-ethyl substituent encourages methyl migration.

In contrast, the reactions of complexes **1b**,**c** with MeI give only the acetyl species [Rh(PN^{Ar})(COMe)I_2] (**3b**,**c**), indicated by ν(CO) absorptions at ca. 1716 cm^{-1}. The presumed intermediate methyl complexes (**2b**,**c**) were not detected during these reactions. Thus, the presence of two ortho alkyl substituents on the iminophosphine N-aryl group promotes migratory CO insertion, as found previously for Rh α-diimine complexes.[3] The ^{1}H NMR spectrum of **3c** displays two septets and four doublets arising from the two inequivalent isopropyl groups, consistent with square-pyramidal coordination geometry with an apical acetyl ligand, as found for related Rh(III) complexes.[2,3,32−35]

A stable Rh(III) acetyl complex, **3e**, was formed by the reaction of MeI with the *o*-anisyl derivative **1e**. Again, the presumed methyl intermediate **2e** was not detected, indicating that methyl migration is rapid. It is notable that although the iminophosphine ligands in **1d**,**e** have very similar steric bulk, migratory insertion is more favored by the *o*-anisyl-substituted ligand. It was suspected that a thermodynamic driving force for migratory insertion might be provided by an intramolecular interaction between the Rh center and a lone pair on the *o*-methoxy group in **3e**. A shift to lower frequency (by ca. 12 cm^{-1}) of ν(C═O) for **3e** compared with the values for **3b**,**c** is consistent with higher electron density at the metal center, resulting from donation from a methoxy lone pair.

A Rh−O interaction was confirmed by an X-ray crystal structure of the pentane solvate of **3e**. Crystals of suitable quality were grown by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of **3e**. The molecular structure is illustrated in Figure 1, and selected geometrical data are given in Table 1.

The coordination geometry around the Rh center in **3e** is a distorted octahedron, with the two iodide ligands occupying mutually cis coordination sites, trans to the P and N donors of the chelating iminophosphine ligand. The Rh−I(1) distance trans to P is ca. 0.09 Å longer than that trans to N, indicating that the PPh_2 moiety has a greater trans influence. This is consistent with the previous observation of longer Rh−I distances in [Rh(diphosphine)(COMe)I_2] complexes[2,32−34] than in [Rh(ArN═C(Me)C(Me)═NAr)(COMe)I_2] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[3] The coordination site trans to the acetyl ligand in **3e** is occupied by the *o*-methoxy group of the iminophosphine. The Rh−O(2) distance (2.539(7) Å) is quite long compared to values of 2.33−2.35 Å recently found for Rh(I) complexes of S,S-dipamp (Ph(2-C_6H_4-OMe)PC_2H_4P(2-C_6H_4-OMe)Ph),[36] suggesting a relatively weak Rh−O interaction in **3e**. Substantial distortions from regular octahedral geometry are apparent in the angles between trans coordinated atoms (e.g., N−Rh−I(2) and C(27)-Rh−O(2)). The acetyl ligand adopts a conformation that minimizes steric interactions with the iminophosphine ligand. This directs the acetyl methyl toward I(2) (C(28)−C(27)−Rh−I(2) torsion angle ca. −28°), and the resulting steric clash displaces I(2) out of the approximate plane defined by Rh, I(1), N, and P. This distortion is also evident from the C(27)−Rh−I(2) angle of 100.6(3)°. The six-membered iminophosphine chelate ring adopts a distorted-envelope conformation with the P atom almost coplanar with the three carbon atoms of the ligand backbone (C(19)−C(6)−C(1)−P torsion angle ca. 1°). The nitrogen and rhodium atoms deviate substantially from this CCCP plane, with torsion angles C(1)−C(6)−C(19)−N = 27.5° and C(6)−C(1)−P−Rh = −38.8°. This conformation is common for chelate rings of this type,[37] and the P−Rh−N bite angle of 86.9(2)° is comparable to values reported for other Rh iminophosphine complexes.[27,28] The Rh−O interaction is facilitated by the conformation adopted by the *o*-anisyl group, the ipso carbon of which is displaced ca. 0.87 Å from the approximate plane defined by Rh, I(1), N, and P. The resulting five-membered chelate ring has an envelope conformation with Rh at the apex and a N−Rh−O(2) bite angle of 68.7(3)°).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3e

Rh−I(1)	2.7502(10)	Rh−C(27)	2.004(11)
Rh−I(2)	2.6569(11)	C(27)−O(1)	1.193(12)
Rh−N	2.106(8)	C(27)−C(28)	1.504(13)
Rh−P	2.255(3)	N−C(19)	1.285(12)
Rh−O(2)	2.539(7)		
C(27)−Rh−N	96.0(4)	N−Rh−O(2)	68.7(3)
C(27)−Rh−P	89.8(3)	N−Rh−I(2)	163.1(2)
C(27)−Rh−I(1)	87.6|(3)	I(1)−Rh−P	177.34(8)
C(27)−Rh−I(2)	100.6(3)	Rh−C(27)−C(28)	118.7(8)
C(27)−Rh−O(2)	161.2(4)	Rh−C(27)−O(1)	119.3(8)
I(2)−Rh−I(1)	91.05(3)	O(1)−C(27)-C(28)	121.8(10)
N−Rh−P	86.9(2)		

Oxidative Addition Kinetics. Kinetic data for the reactions of **1a**−**g** with MeI in CH_2Cl_2 were obtained by monitoring the decay of the ν(CO) absorption of the Rh(I) reactant. Pseudo-first-order conditions were maintained by keeping the [MeI] in large excess compared with [Rh]. A typical series of spectra is illustrated in Figure 2. Plots of absorbance versus time were well fitted by exponential curves, showing that the reactions are first order in Rh(I) complex. Values of the observed pseudo-first-order rate constants (k_{obs}) are listed in the Supporting Information. Plots of k_{obs} versus [MeI] were linear, indicating that the reactions are first order in MeI and therefore second order overall. Second-order rate constants, obtained from the slopes of these plots, are given in Table 2, along with activation parameters derived from Eyring plots of variable-temperature data measured over the range 15−35 °C. The activation

(32) Adams, H.; Bailey, N. A.; Mann, B. E.; Manuel, C. P. *Inorg. Chim. Acta* **1992**, *198*−*200*, 111.
(33) Søtofte, I.; Hjortkjaer, J. *Acta Chem. Scand.* **1994**, *48*, 872.
(34) Moloy, K. G.; Petersen, J. L. *Organometallics* **1995**, *14*, 2931.
(35) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2002**, *21*, 4808.
(36) Drexler, H.-J.; Baumann, W.; Schmidt, T.; Zhang, S.; Sun, A.; Spannenberg, A.; Fischer, C.; Buschmann, H.; Heller, D. *Angew. Chem., Int. Ed. Engl.* **2005**, 1184.
(37) Perez, J.; Martinez, J. F.; Garcia, L.; Perez, E.; Serrano, J. L.; Sanchez, G. *Inorg. Chim. Acta* **2004**, *357*, 3588.

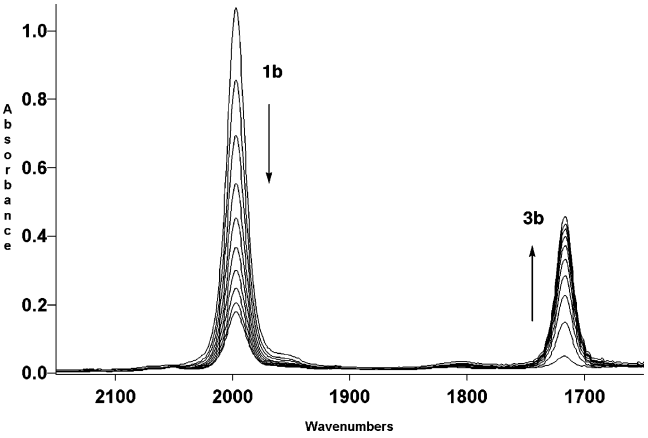


Figure 2. Series of IR spectra recorded during the reaction of **1b** with MeI (CH_2Cl_2, 25 °C).

Table 2. Second-Order Rate Constants (k_1, 25 °C) and Parameters for Oxidative Addition of MeI to Rh(I) Complexes in CH_2Cl_2

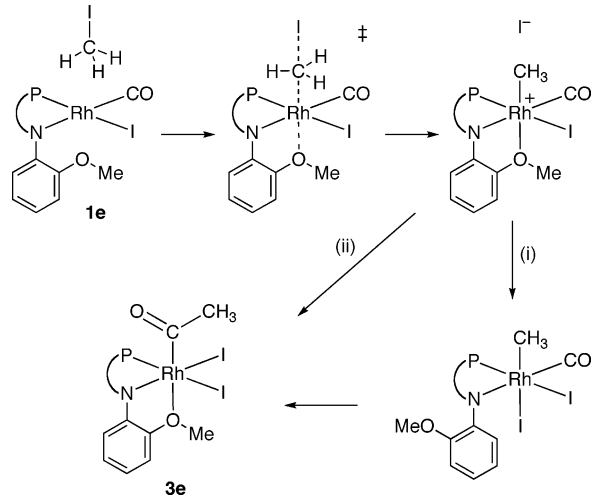
complex	ν(CO)/cm^{-1}	10^4k_1/dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
1a	1998	3.60	51 ± 2	−138 ± 6
1b	1997	7.50	48 ± 1	−145 ± 3
1c	1997	9.10	45 ± 1	−149 ± 3
1d	1997	7.71	55 ± 2	−120 ± 6
1e	1995	31.4	46 ± 1	−138 ± 4
1f	1997	2.61	66 ± 4	−88 ± 14
1g	2002	0.78	54 ± 2	−139 ± 7

entropies are all large and negative, as generally found for oxidative addition of MeI to square-planar d^8 metal complexes, which is considered to proceed via an S_N2 mechanism.[2,3,38−41]

The observed reactivity toward MeI increases the order **1g** < **1f** < **1a** < **1b** ≈ **1d** < **1c** < **1e**. The electron-withdrawing CF_3 groups on the iminophosphine ligand of **1g** clearly reduce the nucleophilicity of the Rh center, as indicated by the higher ν(CO) value for this complex. Notably, the fastest reaction is found for **1e**, which contains an *o*-anisyl substituent. The second-order rate constant for **1e** is 12 times larger than for the *p*-anisyl isomer, **1f**, and 4 times larger than for **1d**, which has an approximately isosteric iminophosphine ligand. We propose that the higher nucleophilicity of **1e** arises from an interaction between the Rh center and a methoxy lone pair, as shown in Scheme 4. The feasibility of such an interaction is demonstrated by the crystal structure of the acetyl product, **3e** (vide supra). It is uncertain whether a Rh−O interaction exists in the ground state of **1e**, although its slightly lower ν(CO) value compared to those for the other Rh(I) complexes studied would be consistent with this.

Scheme 4 shows a mechanism for the reaction of **1e** with MeI. Initial nucleophilic attack by the Rh(I) center will proceed via an S_N2-type transition state to give a cationic Rh(III) methyl intermediate (which was not detected). Two possible pathways are depicted for conversion of this cation to the final product **3e**: (i) displacement of the coordinated methoxy group by iodide, followed by migratory CO insertion and re-formation of the N−O chelate ring, and (ii) methyl migration in the cation,

Scheme 4. Proposed Mechanism for Reaction of 1e with MeI



accompanied by iodide coordination with the N−O chelate ring remaining intact.

Acceleration of MeI oxidative addition by a neighboring group has previously been proposed for Ir(I) Vaska-type complexes. Miller and Shaw found that *trans*-[Ir(CO){PMe_2-(2-$MeOC_6H_4$)}$_2$Cl] reacts with MeI ca. 100 times faster than do the *p*-anisyl and phenyl analogues.[42] More recently, Dutta et al. proposed that Rh−O interactions in Rh complexes of PPh_2(2-$C_6H_4CO_2Me$) can enhance the rates of MeI addition and catalytic methanol carbonylation. Incorporation of *o*-methoxy groups in diphosphine ligands has a significant influence on catalytic performance in a number of other processes: e.g., CO/alkene copolymerization,[43,44] ethene trimerization,[45,46] and asymmetric hydrogenation.[36,47] In the present case MeI oxidative addition to **1e** is an order of magnitude faster than to **1a**,**f**, which is a smaller effect than that found by Miller and Shaw for *trans*-[Ir(CO){PMe_2(2-$MeOC_6H_4$)}$_2$Cl].[42] The more modest acceleration for **1e** may result from additional conformational constraints in the bidentate iminophosphine ligand, which inhibit closer approach of the *o*-methoxy group to the Rh center. This is evident in the relatively long Rh−O distance in the X-ray structure of **3e**.

The complexes with iminophosphine ligands containing ortho alkyl substituents on the N-aryl group show a rather unexpected trend in reactivity. Complex **1c** (k_{rel} = 2.5) reacts marginally faster than the less sterically congested **1b** (2.1) and **1d** (2.15), and all three of these complexes are more reactive than the phenyl derivative **1a** (1.0). This behavior contrasts markedly with that observed for [Rh(CO)(α-diimine)I] complexes, in which ortho alkyl substituents on the N-aryl group cause a substantial (up to 10^3-fold) *decrease* in oxidative addition rate. It is not clear why the reverse trend occurs for the [Rh(CO)-(iminophosphine)I] complexes, but one possibility is that the bidentate ligand can be hemilabile. Formation of a 14-electron species by dechelation of the N-donor would be expected to occur more readily for a bulky N-aryl group. If the 14-electron

(38) Rankin, J.; Benyei, A. C.; Poole, A. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 3771.
(39) Martin, H. C.; James, N. H.; Aitken, J.; Gaunt, J. A.; Adams, H.; Haynes, A. *Organometallics* **2003**, *22*, 4451.
(40) Bassetti, M.; Capone, A.; Mastrofrancesco, L.; Salamone, M. *Organometallics* **2003**, *22*, 2535.
(41) Gaunt, J. A.; Gibson, V. C.; Haynes, A.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 1015.
(42) Miller, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 480.
(43) Drent, E.; Wife, R. L. Eur. Pat. Appl. EP-B222454, 1987.
(44) Verspui, G.; Schanssema, F.; Sheldon, R. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 804.
(45) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858.
(46) Agapie, T.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2733.
(47) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.

Table 3. Summary of Crystallographic Data for $3e \cdot C_5H_{12}$

formula	$C_{33}H_{37}I_2NO_2PRh$
formula wt	867.32
cryst syst	monoclinic
space group	$P2_1/n$
color	red
a (Å)	13.4037(8)
b (Å)	16.9491(11)
c (Å)	14.0277(9)
α (deg)	90
β (deg)	90.975(3)
γ (deg)	90
temp (K)	150(2)
Z	4
final R indices ($I > 2\sigma(I)$)	R1 = 0.0638; wR2 = 0.1407
R indices (all data)	R1 = 0.1425; wR2 = 0.1706
GOF	1.020

Rh species is highly reactive toward methyl iodide, the observed trend could result. Although we found no direct evidence for a chelate ring opening mechanism, hemilability of an iminophosphine ligand has been suggested to occur in Pd(II) allyl complexes.[48] Another possibility, suggested by a reviewer, is that an agostic interaction between the Rh center and an ortho alkyl C−H bond can stabilize the S_N2 transition state for oxidative addition and hence accelerate the reaction.

Apart from the *p*-anisyl derivative, **1e**, the Rh(I) iminophosphine complexes studied here are somewhat less reactive than [Rh(CO)(dppe)I] toward MeI ($k_{obs} = 1.41 \times 10^{-3}$ M^{-1} s^{-1}, 25 °C, CH_2Cl_2[2]). It is slightly surprising that a mixed phosphine−imine donor set imparts lower nucleophilicity than dppe, since [Rh(CO)(α-diimine)I] complexes were found to have generally higher MeI oxidative addition rates than [Rh(CO)(dppe)I] (apart from those with sterically hindered N-aryl groups).[3] This comparison is complicated to some extent, because the iminophosphines used here form six-membered chelate rings, in contrast to the five-membered rings formed by dppe and α-diimines. The different conformational properties of the larger ring might introduce additional factors that influence reactivity. The lower rate for the unsymmetrical ligands might also indicate a mutual influence between P and N donors and relates to the behavior of unsymmetrical ligands in catalysis, which commonly is not linearly related to the behavior of corresponding symmetrical ligands.

Conclusion

A series of rhodium iodo carbonyl complexes containing bidentate iminophosphine ligands has been prepared and characterized. The reactivity of these complexes toward MeI is dependent upon both the steric and electronic properties of the N-aryl substituent of the iminophosphine. Most significantly, both oxidative addition and migratory CO insertion are promoted by an *o*-methoxy group, and it is proposed that this effect arises from an intramolecular interaction between the methoxy oxygen and the Rh center. Such an interaction can enhance the nucleophilicity of the Rh(I) reactant (by stabilization of the S_N2 transition state) as well as providing a driving force for migratory CO insertion. An X-ray crystal structure of the acetyl product provides direct evidence for a Rh−O interaction. Migratory CO insertion can also be promoted by bulky ligands (as found in related systems), but there is an unexpected steric effect on MeI oxidative addition. Moderate acceleration of MeI addition by more bulky ligands can be speculated to arise from hemilability of the iminophosphine.

(48) Faller, J. W.; Stokes-Huby, H. L.; Albrizzio, M. A. *Helv. Chim. Acta* **2001**, *84*, 3031.

Experimental Section

Materials. All solvents used for synthesis or kinetic experiments were distilled and degassed prior to use following literature procedures.[49] Synthetic procedures were carried out utilizing standard Schlenk techniques. Nitrogen and carbon monoxide were dried through a short (20 × 3 cm diameter) column of molecular sieves (4 Å), which was regularly regenerated. The complexes $[Rh(CO)_2Cl]_2$[50] and $[Rh(CO)_2I]_2$[51] were synthesized according to literature procedures. The ligands PN^{Ar} (Ar = C_6H_5, 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$) were prepared using established procedures.[15,25,26] Methyl iodide (Aldrich) was distilled over calcium hydride and stored in foil-wrapped Schlenk tubes under nitrogen and over mercury to prevent formation of I_2. Isotopically enriched ^{13}CO (99% ^{13}C) was obtained from Euriso-top.

Instrumentation. FTIR spectra were measured using a Mattson Genesis Series spectrometer, controlled by WIN-FIRST software running on a Viglen 486 PC. ^1H and ^{31}P NMR spectra were obtained using a Bruker AC250 spectrometer fitted with a Bruker B-ACS60 automatic sample changer operating in pulse Fourier transform mode, using the solvent as reference. Elemental analyses were performed by the University of Sheffield Microanalytical Service using a Perkin-Elmer 2400 CHNS/O Series II elemental analyzer. Mass spectrometry was performed using a Micromass VG-AutoSpec instrument (fast atom bombardment (FAB)) or Micromass LCT instrument (electrospray ionization (ESI)).

Synthesis of Ligands. (a) $Ph_2PC_6H_4CH{=}N(2\text{-}EtC_6H_4)$. (Diphenylphosphino)benzaldehyde (224 mg, 0.772 mmol) and 2-ethylaniline (0.4 cm^3, 3.2 mmol) were dissolved in methanol (20 cm^3) with 2 drops of formic acid before being heated to reflux for 3 h. Rotary evaporation yielded a precipitate, which was extracted with cold methanol and dried under vacuum. Yield: 248 mg (82%). ^1H NMR (CD_2Cl_2): δ 1.00 (t, $^3J_{HH} = 7.5$ Hz, 3H, CH_2*Me*), 2.56 (q, $^3J_{HH} = 7.5$ Hz, 2H, *CH*$_2$Me), 6.35, 6.80−7.70, 8.17 (each m, total 18H, Ar *H*), 8.92 (d, $^4J_{HP} = 5.2$ Hz, 1H, N=C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −13.0 (s). MS (FAB; *m*/*z*): 393 [M^+].

(b) $Ph_2PC_6H_4CH{=}N(3,5\text{-}(CF_3)_2C_6H_3)$. A procedure was employed analogous to that described in (a), using (diphenylphosphino)benzaldehyde (500 mg, 1.7 mmol) and 3,5-bis(trifluoromethyl)-aniline (0.4 cm^3, 2.56 mmol). Yield: 639 mg (74%). ^1H NMR (CD_2Cl_2): δ6.90−7.70, 8.14 (each m, total 17H, Ar *H*), 8.92 (d, $^4J_{HP} = 4.9$ Hz, 1H, N=C*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −10.8 (s).

Synthesis of Rh(I) Complexes. (a) $[RhI(CO)(PN^{Ar})]$ (1a; Ar = C_6H_5). A solution of $Ph_2PC_6H_4CH{=}NPh$ (39 mg, 0.11 mmol) in 10 cm^3 of THF was added dropwise to a THF (10 cm^3) solution of $[RhI(CO)_2]_2$ (31 mg, 0.054 mmol). The resulting orange-red solution was stirred for 2 h. The solvent was removed in vacuo before the product was extracted using 40 cm^3 of pentane. The solvent was removed and the product dried overnight in vacuo. Yield: 24 mg (36%). Satisfactory elemental analysis was not obtained for this compound, despite clean spectroscopic data, presumably due to air sensitivity. IR (ν(CO); CH_2Cl_2): 1998 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.96−7.65 (m, 19H, Ar *H*), 8.02 (bs, 1H, N=C*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.3 (d, $J_{RhP} = 166$ Hz).

(b) $[RhI(CO)(PN^{Ar})]$ (1b; Ar = 2,6-$Me_2C_6H_3$). A procedure was employed analogous to that described for **1a**, using $Ph_2PC_6H_4$-$CH{=}N(2,6\text{-}Me_2C_6H_3)$ (62 mg, 0.16 mmol) and $[RhI(CO)_2]_2$ (46 mg, 0.08 mmol). Yield: 59 mg (56%). Anal. Calcd for $C_{28}H_{24}$-INOPRh: C, 51.64; H, 3.71; N, 2.15. Found: C, 51.57; H, 3.70; N, 2.01. IR (ν(CO); CH_2Cl_2): 1998 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.97 (s, 6H, *CH*$_3$), 6.90−7.65 (m, 17H, Ar *H*), 7.87 (bs, 1H, N=C*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.3 (d, $J_{RhP} = 169$ Hz). MS

(49) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, U.K., 1988.

(50) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 214.

(51) Johnson, B. F. G.; Lewis, J.; Miller, J. R.; Robinson, B. H.; Robinson, P. W.; Wojcicki, A. *J. Chem. Soc. A* **1968**, 522.

(ESI; *m*/*z*): 623 [M^+] − CO, 524 [M^+] − I. A ^{13}CO-labeled sample of **1b** was prepared by briefly bubbling ^{13}CO through a solution of the compound in CH_2Cl_2. IR (ν(^{13}CO); CH_2Cl_2): 1953 cm^{-1}. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.3 (d, $^1J_{RhP}$ = 169 Hz, $^2J_{PC}$ = 12 Hz). ^{13}C{^{1}H} NMR δ 190.8 ($^1J_{RhC}$ = 70 Hz, $^2J_{PC}$ = 12 Hz).

(c) [RhI(CO)(PN^{Ar})] (1c; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$). A procedure was employed analogous to that described for **1a** using $Ph_2PC_6H_4CH$═N(2,6-^{i}Pr$_2$C$_6$H$_3$) (82.6 mg, 0.184 mmol) and [RhI(CO)$_2$]$_2$ (50 mg, 0.087 mmol). Yield: 85 mg (69%). Anal. Calcd for $C_{32}H_{32}INOPRh$: C, 54.33; H, 4.56; N, 1.98. Found: C, 54.60; H, 4.48; N, 2.00. IR (ν(CO); CH_2Cl_2): 1997 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 0.69 (d, 6H, 6.7 Hz, *Me*$_2$CH), 1.29 (d, 6H, 6.7 Hz, *Me*$_2$CH), 2.99 (sept, 2H, 6.7 Hz, Me$_2$C*H*), 7.0−7.2 (m, 4H, Ar *H*) 7.42−7.60 (m, 13H, Ar *H*), 8.00 (d, 2.4 Hz, 1H, N═C*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 40.5 (d, J_{RhP} = 172 Hz). MS (ESI; *m*/*z*): 580 [M^+] − I.

(d) [RhI(CO)(PN^{Ar})] (1d; Ar = 2-EtC$_6$H$_4$). A procedure was employed analogous to that described for **1a**, using $Ph_2PC_6H_4CH$═N(2-EtC$_6$H$_4$) (221 mg, 0.562 mmol) and [RhI(CO)$_2$]$_2$ (160 mg, 0.280 mmol). Yield: 254 mg (70%). Anal. Calcd for $C_{28}H_{24}INOPRh$: C, 51.64; H, 3.71; N, 2.15. Found: C, 51.66; H, 3.43; N, 1.92. IR (ν(CO); CH_2Cl_2): 1997 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ0.75 (t, 3H, CH$_2$*Me*), 2.57 (q, 2H, *CH*$_2$Me), 6.80−7.67 (m, 18H, Ar *H*), 7.97 (d, 1.8 Hz, 1H, N═C*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.4 (d, J_{RhP} = 162 Hz). MS (FAB; *m*/*z*): 623 [M^+] − CO, 524 [M^+] − I.

(e) [RhI(CO)(PN^{Ar})] (1e; Ar = 2-MeOC$_6$H$_4$). A procedure was employed analogous to that described for **1a**, using $Ph_2PC_6H_4CH$═N(2-MeOC$_6$H$_4$) (69 mg, 0.175 mmol) and [RhI(CO)$_2$]$_2$ (50.4 mg, 0.088 mmol). Yield: 38 mg (33%). Anal. Calcd for $C_{27}H_{22}INO_2PRh$: C, 49.64; H, 3.39; N, 2.14. Found: C, 49.44; H, 3.41; N, 1.95. IR (ν(CO); CH_2Cl_2): 1995 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.76 (s, 3H, O*Me*), 6.82−7.60 (m, 18H, Ar *H*), 7.99 (d, 2.1 Hz, 1H, N═C*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 44.5 (d, J_{RhP} = 171 Hz). MS (FAB; *m*/*z*): 625 [M^+] − CO, 526 [M^+] − I, 498 [M^+] − CO − I.

(f) [RhI(CO)(PN^{Ar})] (1f; Ar = 4-MeOC$_6$H$_4$). A procedure was employed analogous to that described for **1a**, using $Ph_2PC_6H_4CH$═N(4-MeOC$_6$H$_4$) (84 mg, 0.21 mmol) and [RhI(CO)$_2$]$_2$ (54 mg, 0.09 mmol). Yield: 101 mg (82%). Anal. Calcd for $C_{27}H_{22}INO_2PRh$: C, 49.64; H, 3.39; N, 2.14. Found: C, 49.46; H, 3.28; N, 2.11. IR (ν(CO); CH_2Cl_2): 1997 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H, O*Me*), 6.78 (m, 4H, Ar *H*), 7.52 (m, 14H, Ar *H*), 7.97 (bs, 1H, N═C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 46.8 (d, J_{RhP} = 168 Hz).

(g) [RhI(CO)(PN^{Ar})] (1g; Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$). A procedure was employed analogous to that described for **1a**, using $Ph_2PC_6H_4$-CH═N(3,5-(CF$_3$)$_2$C$_6$H$_3$) (93.4 mg, 0.19 mmol) and [RhI(CO)$_2$]$_2$ (45.2 mg, 0.08 mmol). Yield: 102 mg (85%). Satisfactory elemental analysis was not obtained for this compound, despite clean spectroscopic data, presumably due to air sensitivity. IR (ν(CO); CH_2Cl_2): 2002 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.90−7.01 (m, 1H, C$_6$H$_2$(CF$_3$)$_2$−*H*), 7.38−7.66 (m, 16H, Ar *H*), 7.92 (bs, 1H, N═C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 46.1 (d, J_{RhP} = 165 Hz). MS (FAB; *m*/*z*): 759 [M^+], 731 [M^+] − CO, 632 [M^+] − I, 604 [M^+] − CO − I.

Synthesis of Rh(III) Complexes. (a) [Rh(COMe)I$_2$(PN^{Ar})] (3b; Ar = 2,6-Me$_2$C$_6$H$_3$). Complex **1b** (15 mg) was dissolved in THF (5 cm^3), and iodomethane (2 cm^3) was added. After the mixture was stirred for 1 h, the volatiles were removed in vacuo to yield a dark orange solid. Anal. Calcd for $C_{29}H_{27}I_2NOPRh$: C, 43.91; H, 3.43; N, 1.77. Found: C, 44.25; H, 3.73; N, 1.58. IR (ν(CO); CH_2Cl_2): 1716 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ2.10 (s, 6H, Me), 3.55 (s, 3H, CO*Me*), 6.78−7.64 (m, 17H, Ar *H*), 8.15 (d, 2.7 Hz, 1H, N═C*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 46.9 (d, J_{RhP} = 131 Hz). MS (FAB; *m*/*z*): 623 [M^+] − COMe − I.

(b) [Rh(COMe)I$_2$(PN^{Ar})] (3c; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$). A procedure analogous to that described above for **3b** was employed. Anal. Calcd for $C_{33}H_{35}I_2NOPRh$: C, 46s.67; H, 4.15; N, 1.65. Found: C, 46.57; H, 4.02; N, 1.55. IR (ν(CO); CH_2Cl_2): 1717 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 0.96, 1.13, 1.16, 1.29 (each d, 3H, $^3J_{HH}$ = 7.6 Hz, CH(*Me*)$_2$), 1.73, 2.55 (each sept, 1H, $^3J_{HH}$ = 7.6 Hz, C*H*(Me)$_2$), 3.28 (s, 3H, CO*Me*), 6.93−7.86 (m, 17H, Ar *H*), 8.17 (d, 3.7 Hz, 1H, N═C*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 46.5 (d, J_{RhP} = 135 Hz). MS (FAB; *m*/*z*): 806 [M^+] − COMe, 722 [M^+] − I, 694 [M^+] − CO − I, 679 [M^+] − COMe − I.

(c) [Rh(COMe)I$_2$(PN^{Ar})] (3e; Ar = 2MeOC$_6$H$_4$). A procedure analogous to that described above for **3b** was employed. Anal. Calcd for $C_{28}H_{25}I_2NO_2PRh$: C, 42.29; H, 3.17; N, 1.76. Found: C, 41.90; H, 3.41; N, 1.65. IR (ν(CO); CH_2Cl_2): 1704 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 3.30 (s, 3H, CO*Me*), 3.93 (s, 3H, O*Me*), 6.65−7.85 (m, 18H, Ar *H*), 8.20 (d, 3 Hz, 1H, N═C*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 44.7 (d, J_{RhP} = 135 Hz). MS (FAB; *m*/*z*): 752 [M^+] − COMe, 625 [M^+] − COMe − I. A crystal suitable for study by X-ray diffraction was obtained by slow diffusion of pentane into a concentrated chloroform solution of **3e**.

X-ray Structure Determination. Data were collected on a Bruker Smart CCD area detector with Oxford Cryosystems low-temperature system using Mo Kα radiation ($\bar{\lambda}$ = 0.710 73 Å). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times the U_{eq} value of the carrier atom. Complex scattering factors were taken from the program package SHELXTL.[52] Crystallographic data are summarized in Table 3, and full listings are given in the Supporting Information.

Kinetic Experiments. Samples for kinetic runs were prepared by placing the required amount of freshly distilled iodomethane in a 5 cm^3 graduated flask, which was then filled up to the mark with CH_2Cl_2. A portion of this solution was used to record a background spectrum. Another portion (typically 500 μL) was added to the solid Rh complex (typically 5−8 μmol) in a sample vial to give a reaction solution containing 10−15 mM [Rh]. A portion of the reaction solution was quickly transferred to the IR cell, and the kinetic experiment was started. Pseudo-first-order conditions were employed, with a least a 10-fold excess of MeI, relative to the metal complex. The IR cell (0.5 mm path length, CaF_2 windows) was maintained at constant temperature throughout the kinetic run by a thermostated jacket. Spectra were scanned in the metal carbonyl ν(CO) region (2200−1600 cm^{-1}) and saved at regular time intervals under computer control. After the kinetic run, absorbance versus time data for the appropriate ν(CO) frequencies were extracted and analyzed off-line using Kaleidagraph curve-fitting software. The decays of the bands of **1a**−**g** were all well fitted by exponential curves with correlation coefficients ≥0.999, to give pseudo-first-order rate constants. Each kinetic run was repeated at least twice to check reproducibility, the k_{obs} values being averaged values with component measurements deviating from each other by ≤5%.

Acknowledgment. We thank the EPSRC and BP Chemicals Ltd. for funding this research (studentship to J.M.W.) and Dr. Glenn Sunley for helpful discussions.

Supporting Information Available: Tables giving kinetic data and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070019B

(52) Sheldrick, G. M. SHELXTL, an Integrated System for Solving and Refining Crystal Structures from Diffraction Data, Revision 5.1; Bruker AXS Ltd., Madison, WI.